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FORMATION AND STABILITY OF NICKEL-ZIRCONIUM GLASSES

Y.D. Dong*, G. Gregan and M.G. Scott

University of Sussex, School of Engineering
and Applied Sciences, Brighton. BN1 9QT.
England.

*On leave from Institute of Metal Research
of the Chinese Academy of Sciences, Shenyang,
China.

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ABSTRACT

Glasses may be formed in two composition ranges: 33 to 42 and 60 to 76at%Zr. The crystallisation temperatures (T_x), activation energies (Q_x), crystallisation morphologies, densities, Young's moduli and peak in the x-ray diffraction pattern (Q_p) are reported as a function of composition. T_x , Q_x and Q_p do not extrapolate smoothly between the two composition ranges. Maximum thermal stability occurs at 36at%Zr, well away from the value predicted by the free electron approach of Nagel and Tauc. The glasses are denser than would be expected from a simple dense random packing of hard spheres. Some implications for the structure of all-metal glasses are discussed.

INTRODUCTION

Rapid solidification (splat-quenching) can lead to the formation of glassy phases in a large number of metal alloys (1). The fascinating properties of these new materials have made them a major area of scientific investigation. Of particular interest have been the ferromagnetic glasses based on iron, nickel and cobalt. These are formed in alloys of the type $T_{100-x} X_x$ where T is one or more transition metals and x one or more metalloids. Glass formation is limited to a few percent either side of the eutectic composition, which in all of these alloys is near $x = 20\text{at}\%$. In this paper we describe glasses of a second type, namely those containing only transition and noble metals. In these systems, of which Cu-Zr is a typical example, the glass-forming range is often large, e.g. from $\text{Cu}_{30}\text{Zr}_{70}$ to $\text{Cu}_{70}\text{Zr}_{30}$ (2), and embraces not only near eutectic compositions but the stoichiometry of intermediate phases. Such materials were originally described as microcrystalline (3) but have now been shown to exhibit mechanical (4), thermal (5) relaxation behaviour (6) similar to that of the metal-metalloid glasses. Recent patent applications (7) have indicated that their high electrical resistivity and their zero or negative temperature coefficients may make these glasses particularly useful for a number of resistive devices, including standard resistances and low temperature thermometers. From a scientific point of view the wide glass-forming range in these alloys enables a detailed examination of the composition dependence of glass-formability, stability and physical properties. We present here the preliminary results of such an investigation into the nickel-zirconium system.

The equilibrium diagram for nickel-zirconium binary alloys contains four well defined eutectics at 8.8, 36.3, 63.5 and 75.9at% zirconium

(fig 1). There is however some uncertainty about the exact stoichiometry of the intermetallic phases present between Ni_7Zr_2 and $\text{Ni}_{10}\text{Zr}_7$. Ray et al (3) first produced glasses between 60 and 80 at%Zr. Subsequently glass formation has been reported at all four eutectic compositions and at the intermediate phase NiZr_2 (9-11). These ranges are marked on fig 1. Little is known about the crystallisation behaviour of Ni-Zr glasses. By examining a few widely separated alloy compositions Buschow et al (11) showed that there was a trend of increasing resistance to crystallisation with increasing nickel content and produced evidence for the formation of a metastable fcc phase in $\text{Ni}_{22}\text{Zr}_{78}$. Likewise, Polyessya et al (9) have described a non-equilibrium phase as the initial devitrification product of the $\text{Ni}_{64}\text{Zr}_{36}$ glass. In this paper we describe the preliminary results of a detailed study of the composition dependence of thermal stability, crystallisation morphology, density and some mechanical properties. Some implications for the structure of the glasses are discussed.

EXPERIMENTAL

Ingots of the binary alloys were made by induction melting high purity zirconium and nickel over a water-cooled silver hearth. Rapid solidification was achieved by melt-spinning onto a copper wheel under an argon atmosphere so as to produce ribbons 20 to 50 μm thick and up to 8mm wide. The compositions and homogeneity of the ribbons were checked by x-ray fluorescence analysis. Pick up of silicon from the crucibles used in melt-spinning was always less than 0.25wt%. Calorimetry was carried out in a Perkin Elmer DSC 2 at heating rates between 1 and 80 K/min. Isothermal heat treatments were carried out in a tube furnace after sealing the

specimens in evacuated quartz tubes. Young's moduli were measured dynamically from the velocity of 150 kHz extensional waves. This technique will be described in detail elsewhere (12). Densities were measured by a modification of the Archimedeian method suitable for small samples (13) using diethyl phthalate as the weighing liquid. The structures of both as-spun and annealed ribbons were examined by x-ray diffraction using $\text{CoK}\alpha$ radiation. For transmission electron microscopy the specimens were thinned either by jet polishing using 80:20 methanol:perchloric acid at -15°C or by the window technique using 7:33:60 perchloric acid:butanol:methanol at -60°C , and examined at 120 kV.

RESULTS

Glasses were obtained within two composition ranges: from 33 to 42 and from 60 to 78 at%Zr. These compositions include three of the four eutectics and two equilibrium phases: $\text{Ni}_{10}\text{Zr}_7$ and NiZr_2 . We were unable to make glasses at the $\text{Ni}/\text{Ni}_5\text{Zr}$ eutectic; ribbons of this composition contained only the equilibrium phases. In all cases the x-ray diffraction patterns of the glasses contained two broad haloes. The positions of the peak of the first halo, Q_p , varied smoothly with composition across each glass forming range (fig 2a). It does not seem that the curves for the two ranges can be smoothly linked with each other. TEM micrographs showed a strongly mottled appearance not reported before in metallic glasses. This structure, which resembles that observed during the phase separation of oxide glasses, was at first believed to indicate the presence of two glassy phases. The diffraction patterns, however, showed the presence of only one phase and we now believe the mottling to be an electro-polishing artefact. Neither chemically

thinned specimens nor those chemically polished before electro-thinning showed this effect.

The densities of the glasses varied smoothly with composition (fig 2(b)), becoming less dense with increasing zirconium content as expected. For comparison the density of one ingot, Zr_2Ni , was determined to be $7.240 \pm 0.005 \text{ gm cm}^{-3}$, which is about 2% denser than the equivalent glass. The gram atomic volume of the glasses varied linearly with composition.

Although the velocity of sound in an individual ribbon was measurable to within $\pm 0.1\%$ there was a variability of several percent between different ribbons of the same alloy. As we will show elsewhere (12) these variations arise from differences in quenching conditions and therefore in the state of relaxation of the as-quenched glass. The Young's modulus of the ribbons was determined from $E = v^2/\rho$ where v was the velocity of the extensional waves and ρ the density. The major error in the values of E is from inaccuracies in the density. Within the constraints mentioned above the Young's modulus fell smoothly with increasing zirconium content (fig 2(c)), thus paralleling the decrease in density and, as shown later, the decrease in thermal stability.

To compare their relative thermal stabilities the glasses were heated at 10 deg min^{-1} in the D.S.C. The onset temperature of the first crystallisation exotherm was taken as the crystallisation temperature (T_x). The peak of the exotherm was designated T_{x1} . In many cases crystallisation was incomplete until after a second or even a third exotherm; these subsequent exotherms were labelled T_{x2} , T_{x3} . Activation energies for crystallisation (Q_x) were

determined from the shift in T_x with heating rate according to the method of Kissinger (14). The variation of T_x and Q_x with composition are plotted in Fig 2(d). Neither extrapolated smoothly between the two composition ranges. To identify the phase transformations associated with each exotherm specimens were heated until the exotherm had started, quenched to room temperature and then examined by x-ray diffraction. The detailed crystallisation behaviour within each of the two composition ranges is discussed separately below.

The composition dependence of the DSC exotherms in 33 to 42 at%Zr glasses is shown in fig 3. At a heating rate of 10 deg min^{-1} all glasses containing less than 36at%Zr exhibited only one large exotherm between 800 and 900K and a much smaller exotherm near 1000K; those with more than 36at%Zr exhibited two exotherms between 800 and 900K with increasing separation as the zirconium content was increased. Both the crystallisation temperature and the activation energy were a maximum at 36at%Zr which is close to the equilibrium eutectic composition. Isothermal anneals confirmed that the thermal stability was a maximum at the equilibrium eutectic composition. Identification of the crystallisation products of these glasses was hindered by a lack of detailed information about the equilibrium phases in this area of the phase diagram. Only the phase $\text{Ni}_{10}\text{Zr}_7$ is well characterised crystallographically (15). Moreover, because they solidify peritectically the master ingots did not contain the equilibrium phases. Thus alloys with stoichiometries Ni_7Zr_2 , Ni_5Zr_2 (the phase has recently been suggested as $\text{Ni}_{21}\text{Zr}_8$ (16)) and $\text{Ni}_{10}\text{Zr}_7$ were carefully homogenised and their diffraction patterns recorded for use as standards. X-ray diffraction patterns from glasses heated to a few degrees above T_x indicated

that in all cases the phase $\text{Ni}_{10}\text{Zr}_7$ was formed during initial crystallisation. In hyper-eutectic alloys diffraction patterns from specimens heated to T_{x2} showed the presence of $\text{Ni}_{10}\text{Zr}_7$ plus reflections due to a second phase. We were unable to match these reflections to either the patterns recorded previously for Ni_5Zr_2 or Ni_7Zr_2 or to that reported in the literature for Ni_3Zr (17). They did, however, match those reported by Polesya et al (9) in annealed $\text{Ni}_{64}\text{Zr}_{36}$ glass. In glasses of hypoeutectic composition the single exotherm corresponded to the simultaneous crystallisation of both $\text{Ni}_{10}\text{Zr}_7$ and the unknown phase.

Isothermal anneals followed by x-ray diffraction and TEM were carried out on several glasses within this composition range. In the simplest case, 42at%Zr, transformation occurred directly to the equilibrium phase $\text{Ni}_{10}\text{Zr}_7$. The crystals had a dendritic morphology and nucleated randomly within the amorphous matrix (fig 4(a)). In hypoeutectic alloys $\text{Ni}_{10}\text{Zr}_7$ and the unknown phase formed simultaneously. In eutectic and hypereutectic alloys specimens which had just started to crystallise contained only the unknown phase. At a later stage crystals of $\text{Ni}_{10}\text{Zr}_7$ also appeared.

The composition range 60 to 78at%Zr contains two equilibrium eutectic compositions (63.5 and 76at%Zr) and the intermediate phase Ni-Zr_2 . This part of the phase diagram is well documented and detailed crystallographic data exist for the phases NiZr and NiZr_2 (18). Fig 5 shows the compositional dependence of the DSC exotherms at a heating rate of 10 deg/min. Both T_x and Q_x fell monotonically with Zr content throughout the composition range. Glasses with composition NiZr_2 and those zirconium rich with respect to this composition exhibited only one sharp exotherm.

At the stoichiometry NiZr_2 this exotherm corresponded to transformation of the glass directly to the equilibrium phase. Fig 5 shows the microstructures obtained during isothermal annealing of this glass. The crystals had no preferred shape but contained a very fine structure which we believe to arise from microtwinning. A detailed study of this structure will be published elsewhere (19). In the zirconium rich glasses the single exotherm arose from the simultaneous formation of the equilibrium phases $\alpha\text{-Zr}$ and NiZr_2 . Between NiZr and NiZr_2 the behaviour was more complicated. At the eutectic composition (63.5at%Zr) it was impossible to separate the processes giving rise to the three overlapping broad exotherms. However, x-ray diffraction patterns taken from specimens heated to various temperatures within the crystallisation range showed only the equilibrium phases. In the 62at%Zr glass where the two exotherms were well resolved the first arose from the crystallisation of NiZr_2 and the second to crystallisation of NiZr from the nickel enriched glass.

Thus far we have described only the formation and stability of fully glassy ribbons. By adjusting the melt-spinning conditions - primarily wheel spin and melt ejection pressure - it was possible to reduce the cooling rate so as to produce partially crystalline material within the described composition ranges. Fig 4(b) shows a typical example in the 42at%Zr alloy. Large spherical crystals of $\text{Ni}_{10}\text{Zr}_7$ are embedded in a glassy matrix of the same composition. It should be noted that this morphology was very different to the dendrites produced by heat-treating the fully amorphous alloy (fig 4(a)). No metastable phases were identified in partially crystalline ribbons of any composition. In all cases one of the equilibrium phases was present; thus 36at%Zr ribbons contained only $\text{Ni}_{10}\text{Zr}_7$ in

addition to the glassy matrix: in the 76at%Zr alloy the only crystals were α -Zr. The influence of quenched-in crystallinity on the stability of the remaining glass is illustrated in Fig 6 which shows DSC traces from two partially crystalline alloys and for comparison those from the equivalent fully glassy alloys. In both cases the crystallisation temperature was lowered by the introduction of subsidiary exotherm at a lower temperature than the main exotherm. The position of the major exotherm was unchanged.

DISCUSSION

The glass forming ranges reported here are in broad agreement with those described elsewhere for this system. With improved quenching techniques there is little doubt that the ranges could be widened; indeed we have succeeded in producing partially glassy material at the composition NiZr. Glass formation in any material is favoured by a high value of the reduced glass temperature $T_{rg} = T_g/T_m$ (where T_g is the glass transition temperature and T_m is the melting point). Davies (20) has shown that for metallic glass formers T_{rg} is generally between 0.4 and 0.6. Taking the crystallisation temperature T_x as a lower limit for T_g the reduced glass temperature for all the alloys considered in this work is greater than 0.4, in agreement with Davies' observations. In metal-metalloid alloys a high T_{rg} is achieved only near a eutectic composition and glass formation occurs only in a narrow composition range near such compositions. In no case have glasses been produced at the stoichiometry of a stable intermediate phase in such alloys. It is clear from the present work that such constraints do not apply in metal-metal systems. Glass formation is easy over a wide

composition range often well away from equilibrium eutectics and even at the local melting point maxima associated with intermetallic compounds. Marcus and Turnbull (21) have suggested that glass forming ability is related to the negative deviation of the liquidus from the ideal solution value. This approach works well for many metal-metalloid glass formers but as shown by Zielinski et al (10) the deviation in the nickel-zirconium system is actually positive for nickel-rich alloys where the most stable glasses are formed. More recently Ramachandrarao (22) has suggested that glass formation is favoured in those metal-metal alloys that have a large negative deviation from ideal volume. As we will show later this condition is met in nickel-zirconium alloys.

The structure of metal-metalloid glasses is well approximated by a dense random packing of the metal atoms with the metalloid atoms filling the interstices (23). By thus prohibiting metalloid-metalloid pairs such models retain the chemical ordering characteristic of the crystalline compounds in these alloys. To date little attention has been paid to the structure of metal-metal glasses. The simplest model is the dense random packing of non-equal size spheres with no account taken for chemical ordering (23). At the other extreme Wang (25) has proposed a structure based on random packing of the Kasper co-ordination polyhedra found in the crystalline intermetallic phases. For simple dense random packing of non-interactive spheres the atomic volume of the glass should vary linearly with composition, with the partial volumes of the two components close to those in the elemental crystalline state (26). Both Cu-Zr and Gd-Co glasses behave in such a fashion (27). Fig 3(b) shows the atomic volumes of the Ni-Zr glasses. The dotted line is a linear extrapolation between the values for hcp Zr (14.02) and fcc Ni(6.59). It is

clear that although there is a linear variation of atomic volume with composition the Ni-Zr glasses are in fact somewhat denser than would be expected from a simple hard sphere model. The major contribution to this densification is a substantial decrease in the partial atomic volume of the nickel from its equilibrium value of 6.59 to 6.20. The value for zirconium is close to the elemental value. Such behaviour is not entirely unexpected since in all crystalline Ni-Zr compounds the atomic packing is denser than would be predicted from the Goldschmidt radii of Ni and Zr (15,28). This densification is a consequence of a strong Ni-Zr interaction resulting from charge transfer from zirconium to nickel. Waseda and Chen (29) have shown that in the glass $\text{Ni}_{30}\text{Zr}_{70}$ both the Zr-Zr and the Ni-Zr interatomic distances are less than expected. These results are all consistent with a strong Ni-Zr interaction within the glass, suggesting that some short range chemical ordering may be present. Mossbauer spectroscopy has shown such ordering in both Y-Fe (30) and Zr-Fe (31) glasses. The apparent failure of the Q_p versus composition curves for the two glass forming ranges to extrapolate into each other (fig 2(a)) may suggest that the nature of the short range order is different in the two cases. It should be mentioned briefly that unlike Ni-Zr glasses, Cu-Zr glasses behave exactly as expected from a dense random packing of hard spheres: the partial atomic volumes are close to the elemental values (27), the interatomic distances are those expected from the Goldschmidt radii (24) and there is no evidence of chemical ordering. The absence of strong Cu-Zr interactions is undoubtedly a consequence of the complete copper d shell and thus negligible charge transfer from zirconium.

There appears to be no correlation between the crystallisation temperatures of the nickel and zirconium rich glass forming ranges,

an observation which gives some credence to the view that the two glass-forming regions are in fact based on different states of short range order. In metal-metalloid glasses maximum stability against crystallisation is usually at the equilibrium eutectic composition. In the nickel rich glasses considered here the same behaviour holds. there is a maximum T_x at 36.3at%Zr which is the eutectic composition between Ni_5Zr_2 and $Ni_{10}Zr_7$. The stability of the zirconium-rich glasses, however, decreases monotonically with zirconium content with no apparent discontinuities associated with features of the equilibrium diagram. Nagel and Tauc (32) have proposed that for metal-metalloid glasses, at least, maximum stability should occur at a composition such that $Q_p = 2k_f$ where k_f is the Fermi wave number. Using a nearly free electron approach Buschow and Beekmans (11) showed that the electrical properties of Ni-Zr glasses were consistent with a valency of 2 for each zirconium atom. Accordingly k_f was calculated from $k_f = (3\pi^2 N \rho \bar{Z} \bar{A})^{1/3}$ where N is Avogadro's number, \bar{A} , \bar{Z} the weighted atomic numbers and valencies and ρ the measured density) taking Z_{Zr} as 2 and Z_{Ni} as 0.6. The calculated k_f values were compared with the measured Q_p values. Such an approach predicts a maximum stability at $\sim 56\text{at}\%Zr$ well displaced from the measured value. However, as we have shown above, allowance should be made for charge transfer from zirconium to nickel. The exact magnitude of this is uncertain and it is clear that some direct measurements of k_f are required to test the applicability of Nagel and Tauc's approach to metal-metal glasses.

The crystallisation morphologies and kinetics of these glasses will be discussed in detail elsewhere. In the zirconium rich glasses transformation occurs directly to the equilibrium phases with no evidence of the bcc phase reported earlier. The composition

NiZr_2 offers a unique opportunity to study in detail the massive transformation of a glass to a stable crystalline compound, and such studies are underway. The nickel rich glasses transform by way of a metastable phase which though reported previously is as yet unidentified. The role of metastable crystalline phases as intermediaries in the crystallisation of metallic glasses is well established in the case of metal-metalloid systems. What is not yet clear is why during isothermal anneals the metastable phase forms prior to $\text{Ni}_{10}\text{Zr}_2$, yet during dynamic crystallisation the reverse is true. The influence of quenched-in crystals on the thermal stability of the remaining matrix is an area which warrants further investigation. We have shown here that in two alloys 36at%Zr and 42at%Zr ($\text{Ni}_{10}\text{Zr}_7$) the effect of partial crystallinity is to introduce a subsidiary exotherm in the DSC trace at a lower temperature than the major exotherm. Quenched in crystals can destabilise the remaining glass in a number of ways: (a) they can simply grow at a lower temperature than that required for the homogeneous nucleation and growth of crystals in the glassy matrix, (b) they can act as heterogeneous nucleation sites, (c) if the quenched in crystals are due to primary solidification the glass adjacent to the crystals will be enriched in solute and may therefore crystallise at a lower temperature. In the case of the 42at%Zr glass the crystals have the same composition as the matrix and thus only mechanisms (b) or (c) are applicable. In the 36at%Zr glass rejection of either Ni or Zr would lower the glass stability and hence any of the three mechanisms would yield the experimental observations. Observations on other glasses have indicated that growth of quenched in crystals is minimal and that nucleation on these crystals occurs by either (b) or (c) above.

CONCLUSIONS

Glasses may be formed between 33 and 42 and 60 and 78at%Zr. The densities of the glasses are not consistent with a simple dense random packing of spheres. Crystallisation of the zirconium rich glasses occurs directly to the stable phases. In the nickel rich glasses metastable acrySTALLINE phase is formed.

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FIGURE CAPTIONS

- Fig 1 Equilibrium diagram and glass forming ranges for binary nickel-zirconium alloys. Only those phases referred to in text are labelled. Glass forming ranges in present work are at bottom of the diagram.
- Fig 2 Compositional variation of (a) Q_p (b) ρ and \bar{V} (c) Young's modulus (d) T_x and E_x for nickel-zirconium glasses.
- Fig 3 Compositional dependence of the DSC exotherms in glasses containing 33 to 42at%Zr.
- Fig 4 Crystals of $Ni_{10}Zr_7$ produced in 42at%Zr glass
(a) after isothermal annealing
(b) during initial splat-quenching.
- Fig 5 Composition dependence of the DSC exotherms in glasses containing 60 to 78at%Zr.
- Fig 6 Crystal of $NiZr_2$ formed during isothermal annealing of 66.6at%Zr glass.
- Fig 7 Effect of quenched in crystallinity on the DSC traces of (a) 36at%Zr, (b) 42at%Zr glasses.

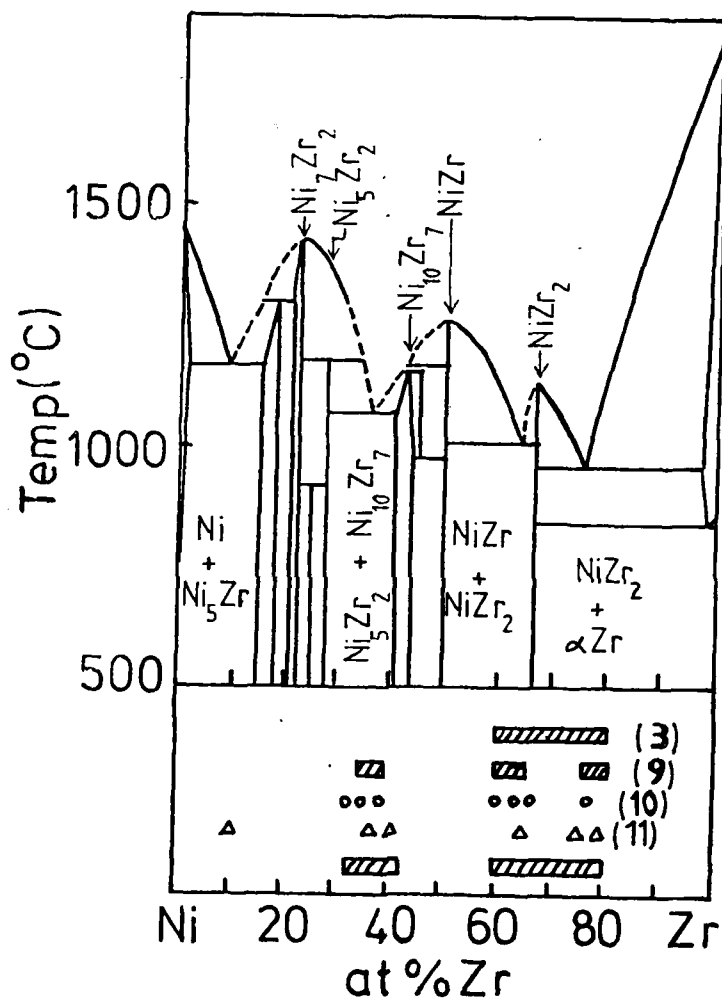


Fig 1.

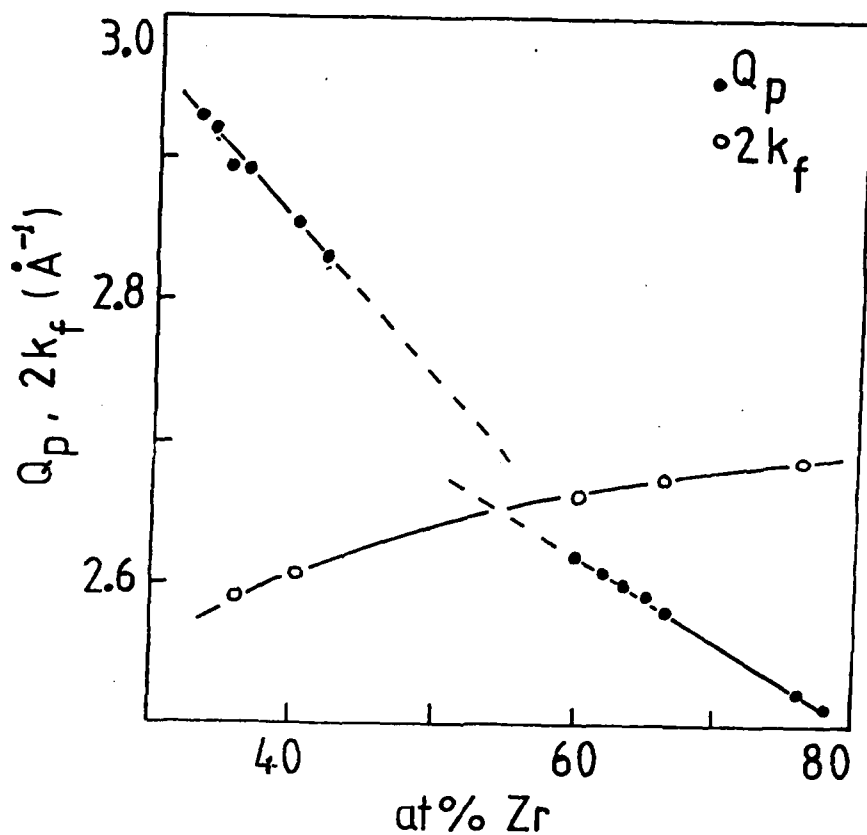


Fig 2(a)

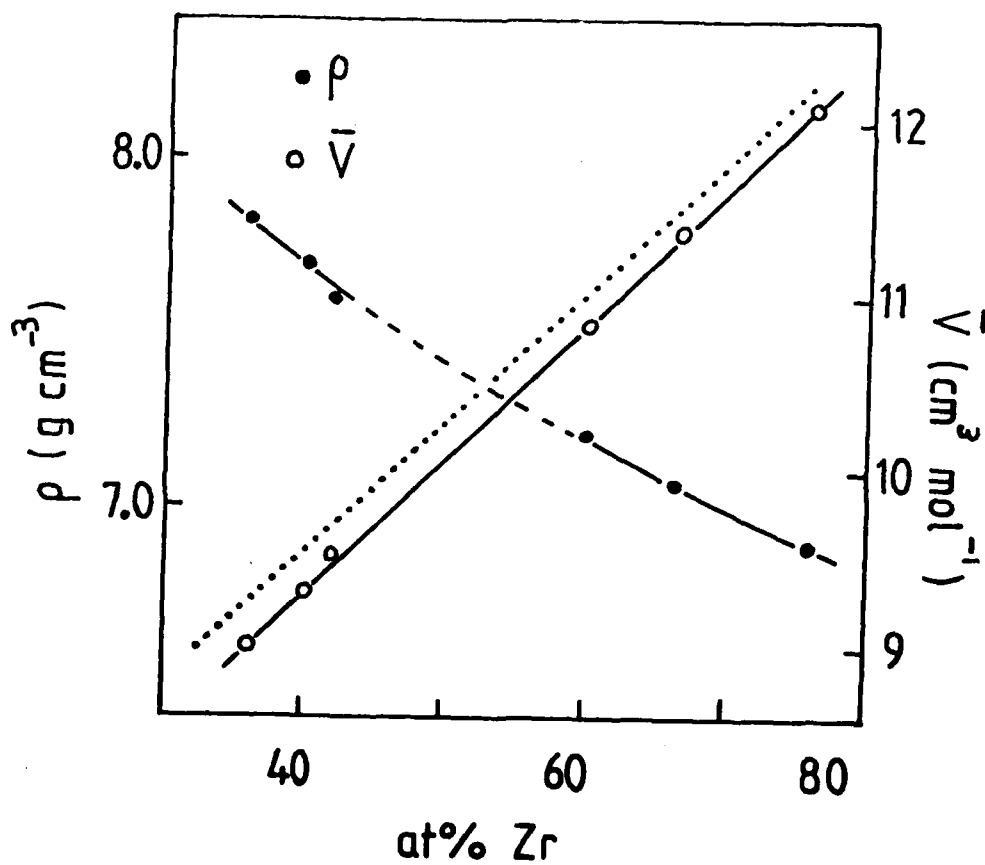


Fig 2(b)

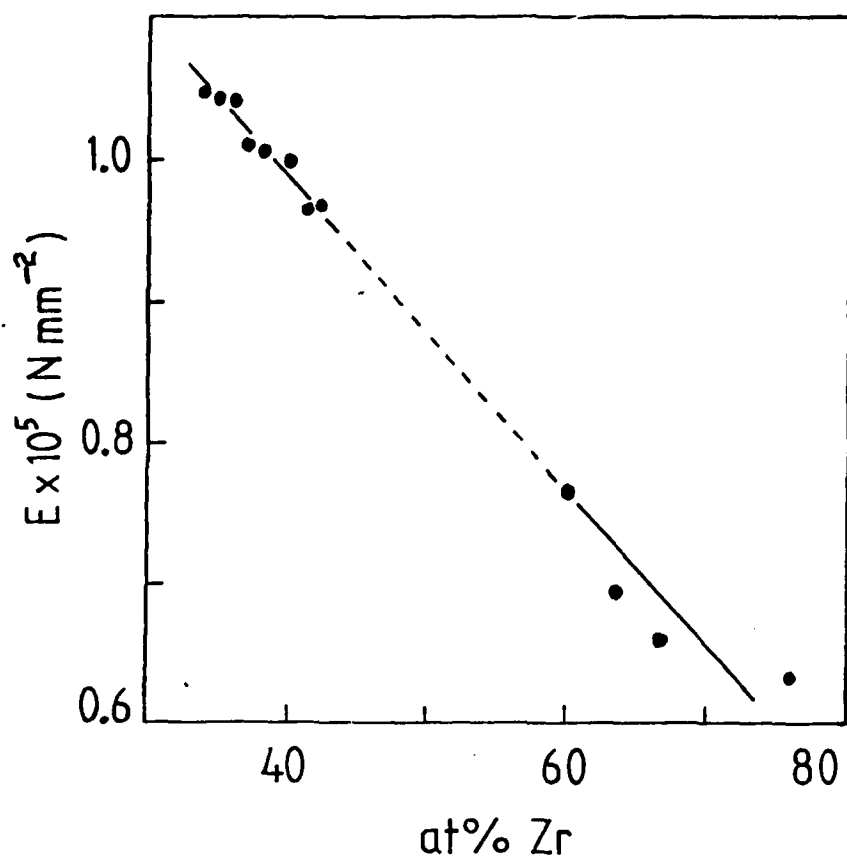


Fig 2(c)

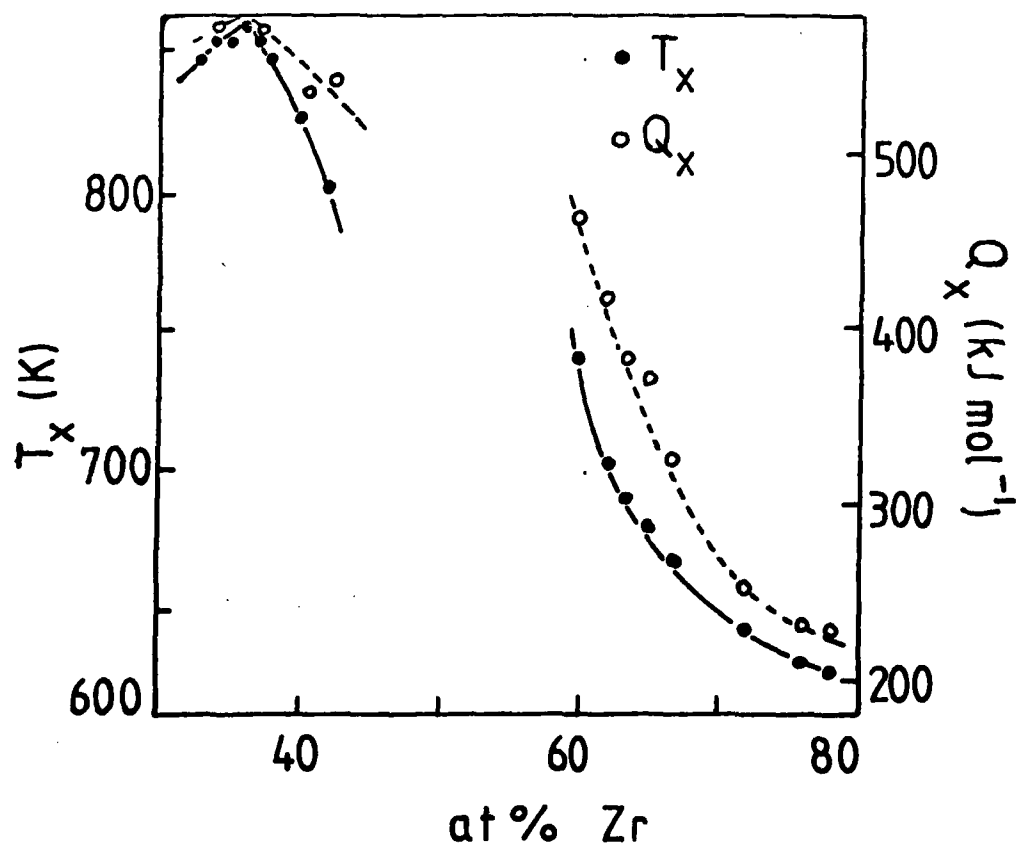


Fig 2(d)

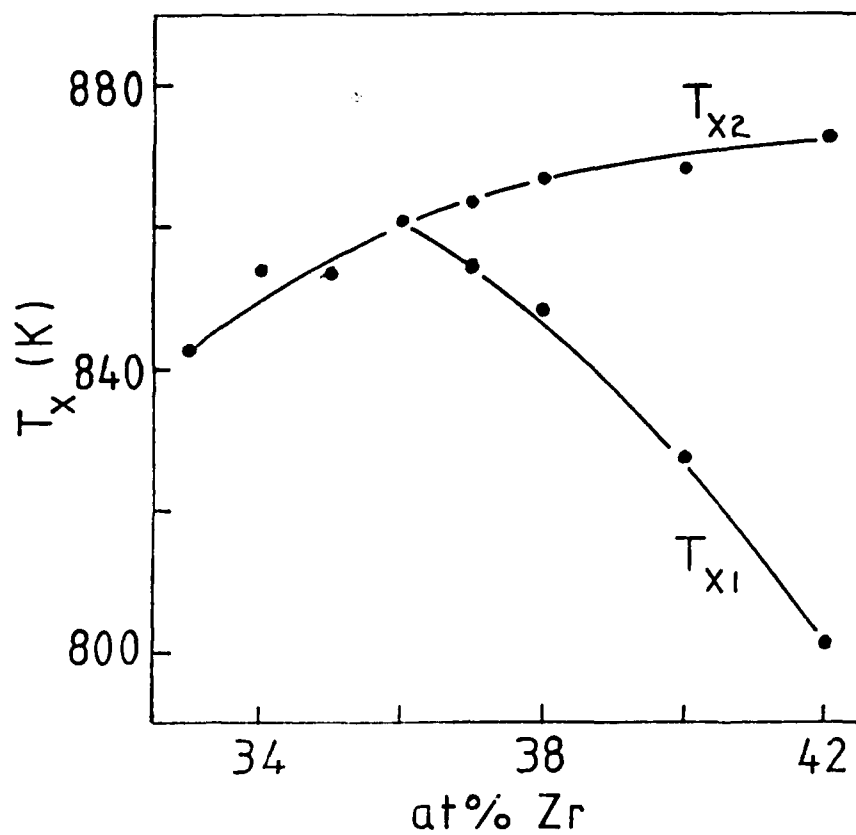
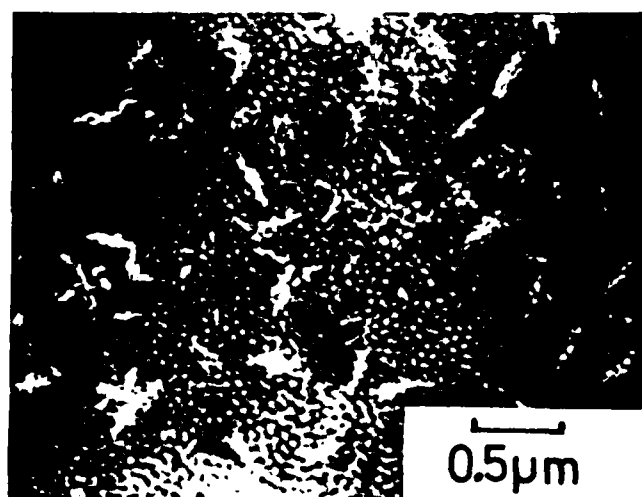
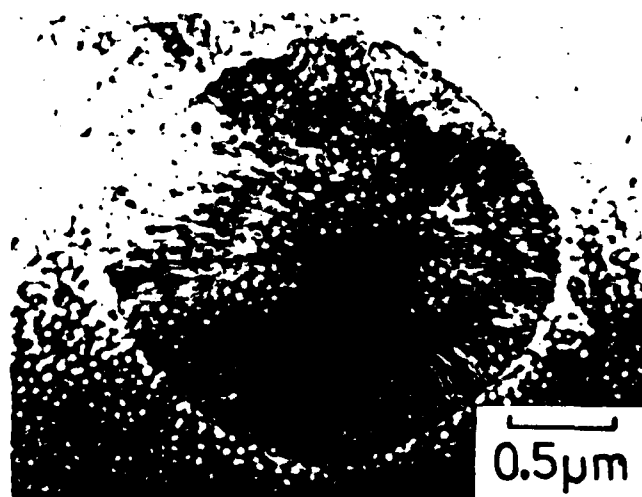


Fig 3



(a)



(b)

Fig 4.

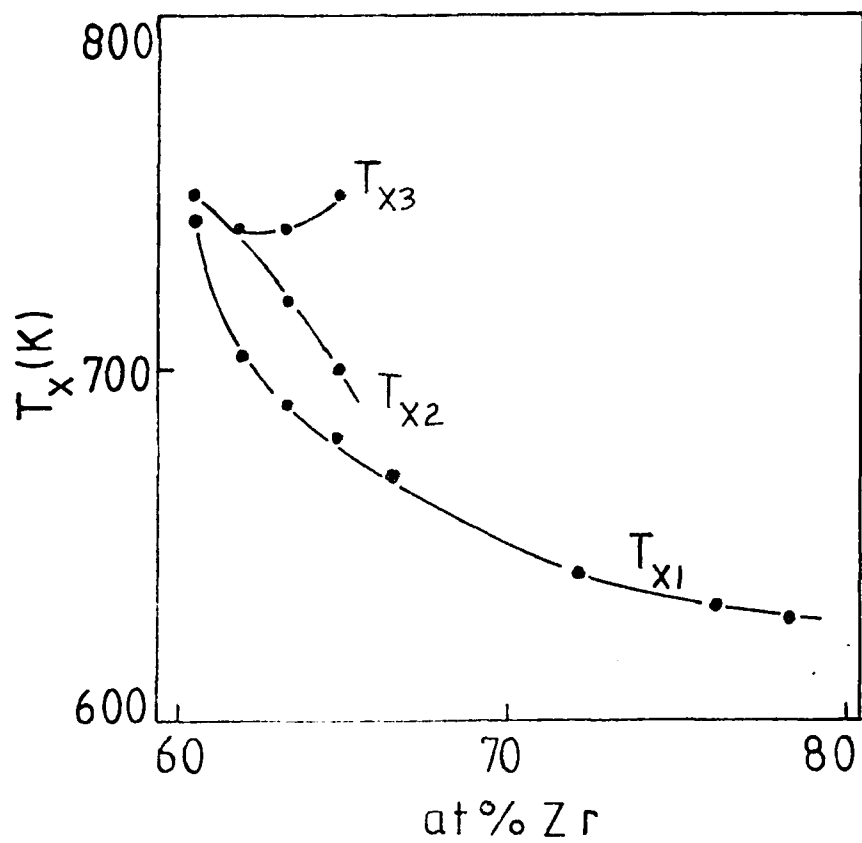


Fig 5

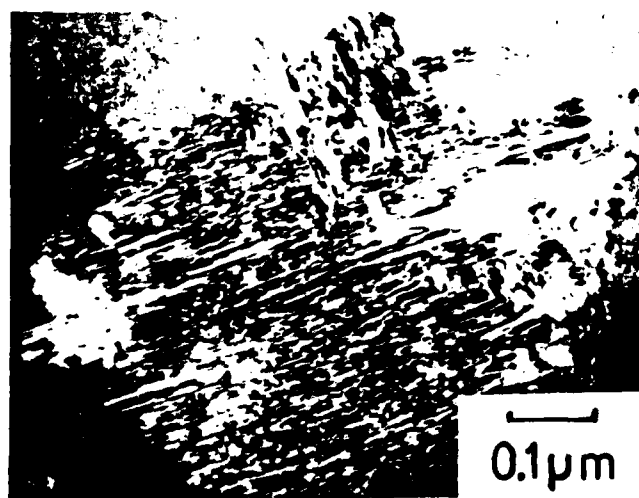
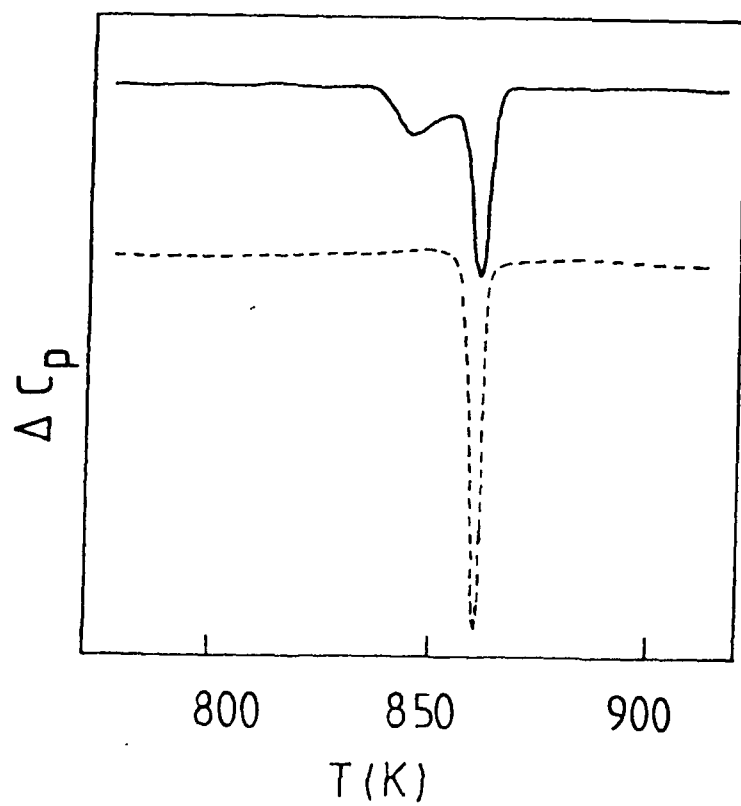
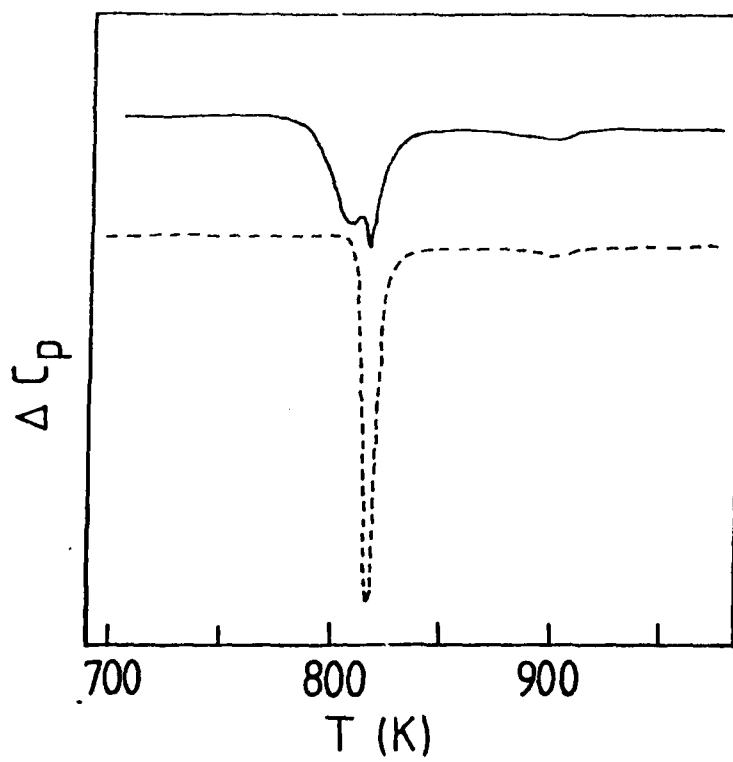


Fig 6.



(a)



(b)

Fig 7

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